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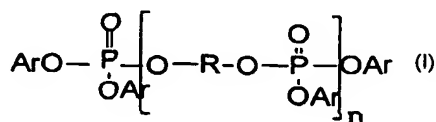
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(54) Title: LOW ACIDITY PHOSPHATE ESTERS



(57) Abstract: A phosphate ester composition of-low acidity achieved by treating the phosphate ester of high acidity with an oxetane compound. The phosphate ester can be represented by the formula (I), where Ar is an aryl or alkaryl group, R is an arylene or alkylene group, and n can range from 0 to about 5.

LOW ACIDITY PHOSPHATE ESTERS

Aromatic oligomeric phosphates, which are used as
5 flame-retardants for thermoplastic resins, are made by
reaction of POCl₃ with a biphenol followed by reaction with
phenol (or by the reaction of diphenyl chlorophosphate with
a biphenol) in the presence of a Lewis acid catalyst to
thereby produce a crude phosphate product. Usually,
10 extensive washing of such a product is needed to remove the
catalyst and other acidic impurities that may negatively
impact the properties of polymers (i.e., polycarbonates,
polyesters, etc.) in which the phosphate ester is placed.
Alternatively, the use of epoxides after removal of the
15 catalyst to decrease acidity has been described in U.S.
Patent No. 5,616,768 and in PCT International Patent
Application No. PCT/US02/03522, filed Feb. 8, 2002.

It has been found that oxetanes are effective in
decreasing the acidity of such phosphate esters. Moreover,
20 it has also been found that an oxetane-treated phosphate
ester showed superior hydrolytic stability when compounded
with a polycarbonate/ ABS resin. While U.S. Patent No.
4,102,859 teaches the combination of neutral esters of
phosphorous acid (i.e., phosphites) and oxetane compounds in
25 plastics, particularly polycarbonate, it does not suggest
the combination of phosphate esters and oxetane compounds.

The phosphate ester can be represented by the
formula:

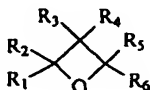


where Ar is an aryl or alkaryl group, R is an arylene or alkylene group, and n can range from 0 to about 5.

Representative R groups include moieties derived from bisphenol A, resorcinol, or neopentyl glycol.

5 The acid number of the phosphate ester used in the present invention is about 5 mg. KOH/g. or less (for example, about 1 mg. of KOH/g. or less, such as about 0.5 mg. of KOH/g. or less). When the acid number exceeds about 5 mg. of KOH/g., a large amount of oxetane may be needed to
10 obtain the desired low acidity, and this can result in a decrease in flame retardancy of the resin.

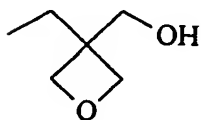
The oxetane compound of the present invention is a compound having one or more oxetane groups and is represented by the general structure:



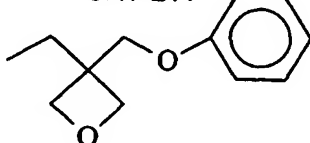
15 In the above structure, R1- R6 are the same or different and can be selected from hydrogen, alkyl or substituted alkyl, aryl or substituted aryl. Examples of such compounds include: 3-ethyl-3-hydroxymethyl-oxetane (OXT-101 brand,
20 available from Toagosei Co., Ltd.); 3-ethyl-3-((phenoxy)methyl)-oxetane (OXT-211 brand, available from Toagosei Co., Ltd.); and 3-ethyl-3-((2-ethylhexyloxy)methyl)-oxetane (OXT-212 brand, available from Toagosei Co., Ltd.).

25 Of these, the OXT-101 oxetane product is particularly preferred because of its low molecular weight and the increased reactivity it provides. Depicted below are the formulae for these products:

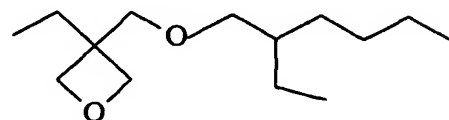
30 OXT-201



OXT-211



OXT-212



5 The number of equivalents of oxetane compound in combination with the phosphate ester can be equal to or greater than the number of equivalents of acid present in the crude phosphate ester based on the acid number of that phosphate ester. The crude phosphate ester to be treated in accordance with the present invention can be heated with the selected oxetane compound at temperature ranging from about 40°C to about 250°C.

10 The present invention is further illustrated by the following Examples.

Example 1

To 203.7 g. of Bisphenol A bis(diphenyl phosphate),
5 having an acid number of 0.555 mg. KOH/g, was added, with
stirring at 110°C, 1.0 g. of 3-ethyl-3-hydroxymethyl-
oxetane (OXT-101 brand from Toagosei Co., Ltd.). After
four hours, the acid number of the resulting phosphate was
0.169 mg. KOH/g.

10

Example 2

To 200 g. of Bisphenol A bis(diphenyl phosphate),
having an acid number of 0.555 mg. KOH/g, was added, with
15 stirring at 140°C, 1.0 g. of 3-ethyl-3-hydroxymethyl-
oxetane (OXT-101 brand from Toagosei Co., Ltd.). After
four hours, the acid number of the resulting phosphate was
0.062 mg. KOH/g.

20

Example 3

To 1005.8 g. of Bisphenol A bis(diphenyl phosphate),
having an acid number of 0.531 mg. KOH/g, was added, with
stirring at 140°C, 5.0 g. (0.043 mole) of 3-ethyl-3-
25 hydroxymethyl-oxetane (OXT-101 brand from Toagosei Co.,
Ltd.). After four hours, the acid number of the resulting
phosphate was 0.060 mg. KOH/g.

Example 4

30

To 1099.9 g. of Bisphenol A bis(diphenyl phosphate),
having an acid number of 0.537 mg. KOH/g, was added, with
stirring at 140°C, 8.3 g. (0.043 mole) of 3-ethyl-3-
(phenoxy)methyl-oxetane (OXT-211 brand from Toagosei Co.,
35 Ltd.). After four hours, the acid number of the resulting
phosphate was 0.14 mg. KOH/g.

Example 5

To 1231.9 g. of Bisphenol A bis(diphenyl phosphate), having an acid number 0.537 mg. KOH/g, was added, with stirring at 140°C, 12.1 g. (0.053 mole) of 3-ethyl-3-((2-ethylhexyloxy)methyl)-oxetane (OXT-212 brand from Toagosei Co., Ltd.). After four hours, the acid number of the resulting phosphate was 0.14 mg. KOH/g.

Examples 5 - 10

Composites of PC/ABS (in a 4:1 ratio), each containing 12.5% of Bisphenol A bis(diphenyl phosphate), were prepared by melt kneading using a twin screw extruder and pelletizing. The pellets were dried for twelve hours at 70°C; then were exposed to 100% humidity atmosphere at 107°C for ninety hours. The change in molecular weight of the polycarbonate was measured after that time. A lower number indicates an increased degree of hydrolytic stability. The results are summarized in Table 1, with Nos. 3-5 relating to the products described in Examples 3-5, above:

Table 1

PC/ABS pellets Containing Sample:	mg. KOH/g. of Sample	% Change in Molecular Weight of PC Resin after 90 hrs.
1 (untreated)	0.5	63
2 (commercial)	0.05	25
3 (OXT-101)	0.06	12
4 (OXT- 211)	0.14	30
5 (OXT- 212)	0.14	25

25

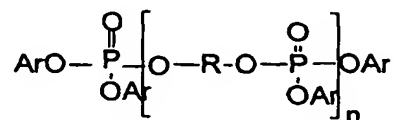
The foregoing Examples are set forth to merely provide certain preferred embodiments of the present invention and, for that reason, should not be construed in a limiting sense. The scope of protection sought is set forth in the Claims that follow.

30

We Claim:

1. A phosphate ester composition of low acidity comprising an oxetane compound.

2. A composition according to Claim 1, in which the phosphate ester is represented by the formula:



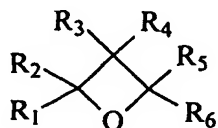
where Ar is an aryl or alkaryl group, R is an arylene or alkylene group, and n can range from 0 to about 5.

3. A composition according to Claim 2 where Ar is phenyl and -O-R-O- is a bisphenol A moiety.

4. A composition according to Claim 2 where Ar is phenyl and -O-R-O- is a resorcinol moiety.

5. A composition according to Claim 2 where Ar is phenyl and -O-R-O- is a neopentyl glycol moiety

6. A composition according to Claim 1, in which the oxetane is represented by the formula:



where R_1 to R_6 are each the same or different and are selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, and substituted aryl.

- 5 7. A composition according to Claim 1 in which the oxetane compound is 3-ethyl-3-hydroxymethyl-oxetane.
8. A composition according to Claim 1 in which the number of equivalents of oxetane compound is equal to
10 or greater than the number of equivalents of acid present in the crude phosphate ester based on the acid number of the crude phosphate ester.
9. A flame-retardant thermoplastic composition
15 containing the phosphate ester composition of Claim 1.
10. A process for decreasing the acidity of a phosphate ester which comprises treating a phosphate ester of acid number greater than 0.1 mg. KOH/g. with
20 an oxetane compound at elevated temperature.
11. A process according to Claim 10 in which the phosphate ester is heated with the oxetane at temperature ranging from about 40°C to about 250°C.
25
12. A process according to Claim 10, in which the phosphate ester is represented by the formula:



where Ar is an aryl or alkaryl group, R is an arylene or alkylene group, and n ranges from 0 to about 5.

- 35 13. A process according to Claim 12 where Ar is phenyl and -O-R-O- is a bisphenol A moiety.

14. A process according to Claim 12 where Ar is
phenyl and
-O-R-O- is a resorcinol moiety.

5

15. A process according to Claim 12 where Ar is
phenyl and
-O-R-O- is a neopentyl glycol moiety.

10

16. A process according to Claim 10 in which the
oxetane compound is 3-ethyl-3-hydroxymethyl-oxetane.

15

17. A process according to Claim 10 in which the
number of equivalents of oxetane compound is equal to
or greater than the number of equivalents of acid
present in the crude phosphate ester based on the acid
number of the crude phosphate ester.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08K5/00 C07F9/12 C07D305/06 C08K5/1525 C08K5/526		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08K C07F C07D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
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Date of the actual completion of the international search 22 October 2003		Date of mailing of the international search report 04/11/2003
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International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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